Dissociation and Isomerization of Vibrationally Excited Species. III*

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The equations of Part I for the specific and over-all unimolecular reaction-rate constants are extended slightly by including centrifugal effects in a more detailed way and by making explicit allowance for possible reaction-path degeneracy (optically or geometrically isomeric paths). The expression for reaction-path degeneracy can be applied to other types of reactions in discussions of statistical factors in reaction rates.

ISOMERIZATIONS or other reactions in which bonds are formed as well as broken are usually expected to involve rigid activated complexes. Reactions involving only a dissocation for which the reverse reaction of recombination requires no activation energy are expected to involve loose activated complexes.[1] In a loose activated complex the dissociated particles are assumed to rotate relatively freely, being held only by loose bonds. By contrast, a rigid complex normally has no new rotations, and indeed has about the same extension in space.

The present paper extends Parts I[2] and II[1] slightly in two respects: (1) Centrifugal effects are treated in a more detailed way. (2) "Optically isomeric" and "geometrically isomeric" *reaction paths* sometimes occur and are included explicitly . The centrifugal effect yields a result which differs slightly from that given earlier[1] for loose activated complexes (a numerical factor of 2 or so). The effect is essentially negligible for rigid complexes. We employ the notation given in Appendix I.

Because of the increased separation distance the centrifugal potential facilitates reaction in any given rotational state of the molecule A. We ignore Coriolis effects and denote by J the totality of quantum numbers that are approximately conserved on forming A^+ from A*. (This J is the quantum number of the "adiabatic" degrees of freedom[3] which, in applications, have usually been taken to be the external rotations of the molecule.) The energy for these degrees of freedom changes from E_J to E_J^+. When the J refers only to rotations, the difference $E_J-E_J^+$ represents the change in centrifugal potential. We have the following energy balance (Fig. 1):

$$E_a+E^+=E_J^++E_J, \tag{1}$$

$$E^+=E_t^++E_n^+. \tag{2}$$

The principal assumptions of the theory have been summarized previously.[1] One finds that k_{EJ}, the specific dissociation-rate constant of molecules of energy E is given by (3) (Appendix II):

$$k_{EJ}=\sum_g \alpha \sum_{E_n^+\leq E^+} \Omega^+(E_n^+)/h\Omega^*(E), \tag{3}$$

where the summation in (3) is over all E_n^+'s and over all geometrically isomeric paths[4] g.

The equilibrium probability of finding an A* with an energy of the active modes in the energy range E, $E+dE$, and with adiabatic modes in the state J is $p_{EJ}{}^o dE$.[5] However, if ω denotes the specific collisional deactivation rate (time^{-1}), the usual steady-state arguments for A* show that the concentration of each A* is a fraction, $k_{EJ}/(\omega+k_{EJ})$, of the equilibrium concentration.[6] Thus, the unimolecular reaction-rate constant k_{uni}, obtained by summing

$$k_{EJ}p_{EJ}{}^o dE/[1+(k_{EJ}/\omega)]$$

over all E and J, is

$$k_{\text{uni}}=\int_E \sum_{J=0}^{\infty} k_{EJ}p_{EJ}{}^o/[1+(k_{EJ}/\omega)]dE. \tag{4}$$

On using Eq. (1) and expressions for $p_{EJ}{}^o$ and k_{EJ} one obtains

$$k_{\text{uni}}=\frac{kT}{hP}\int_{E^+=0}^{\infty}\sum_{J=0}^{\infty}\left[\sum_g\left(\frac{\alpha}{\sigma^+}\right)\exp\left(-\frac{E_a}{kT}\right)\sum_{E_n^+\leq E^+}W^+(E_n^+)\left\{\exp-\frac{(E^++E_J^+)}{kT}\right\}\Big/\,1+\frac{k_{EJ}}{\omega}\right]\frac{dE^+}{kT}. \tag{5}$$

The k_{uni} for formation of a particular product by a particular path g is obtained from (5) by deleting the $\sum_g$ in (5) but not that in (3).

These equations can be simplified for typical conditions as follows. $\Omega^*(E)$ equals $W^*(E)/\sigma$. In turn, $W^*(E)$ equals $W^*(E^*+E_J^+-E_J)$ in virtue of Eq. (1) and the definition of $E^*(=E^++E_a)$. Since $W^*(x)$ is

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[1] G. M. Wieder and R. A. Marcus, J. Chem. Phys. **37**, 1835 (1962) (Part II).

[2] R. A. Marcus and O. K. Rice, J. Phys. & Colloid Chem. **55**, 894 (1951); R. A. Marcus, J. Chem. Phys. **20**, 359 (1952) (Part I). Extensive references to various results are given by M. J. Pearson and B. S. Rabinovitch, *ibid.* **42**, 1624 (1965).

[3] For the definition of active and adiabatic modes compare Part I or Footnote 15 of Part II.

[4] R. A. Marcus, J. Chem. Phys. **43**, 1598 (1965) contains a discussion of reaction-path degeneracy: There may be one or more reaction paths which are "geometric isomers" of each other. For each such path there may be a further degeneracy: a path may have an optical isomer. Optically isomeric reaction paths can be detected by drawing a picture of the chemical migration of the atoms and seeing if the resulting figure has an optical isomer. In Part II α was less accurately called the number of isomers of A^+. That definition is misleading or wrong when two optically isomeric paths intersect in configuration space at A^+ to yield an optically inactive A^+.

[5] $p_{EJ}{}^0=P^{-1}\,\Omega^*(E)\,\exp[-(E+E_J)/kT]$.

[6] This result is obtained in the usual way by assuming a steady-state concentration for A* and assuming in addition a strong collision mechanism for deactivation of A*.

proportional to $(x+aE_o)^{s'-1}$, where a is a quantity which depends weakly on x and approaches unity as x becomes large[7] and where s' is an equivalent number of active modes,[8] we have

$$W^*(E^*+E_J^+-E_J)/[W^*(E^*)] = [1+(E_J^+-E_J)/E^*+aE_o]^{s'-1}. \quad (6)$$

For rigid activated complexes, E_J and E_J^+ are normally about equal, and the ratio of W^*'s in (6) is very close to unity. For loose activated complexes leading to a dissociation, E_J^+ and E_J differ primarily for two rotations in which the two resulting fragments are treated as the "atoms" of a diatomic molecule: The mean value of $E_J^+-E_J$ can be shown to be pressure insensitive and to equal $(I^+-I)lRT/2I$, where l is the number of adiabatic rotations and I^+/I is the ratio of the moments of inertia for these rotations.[9] The value of k_{EJ} is relatively insensitive to fluctuations of $E_J^+-E_J$ about this mean, and the corresponding value of k_{EJ} obtained by making this replacement for $E_J^+-E_J$ is denoted by k_a, for the given value of E^+:

$$k_a=\sum_g(\alpha\sigma/\sigma^+)\Big[\sum_{E_n^+\leq E^+} W^+(E_n^+)\Big]/hW^*(E^*)F, \quad (7)$$

where

$$F=W^*(E^*+lRT[I^+-I]/2I)/W^*(E^*). \quad (8)$$

In Part II k_a was used to denote (7) with F replaced by unity (F was neglected) and with $\sum_g$ absent.

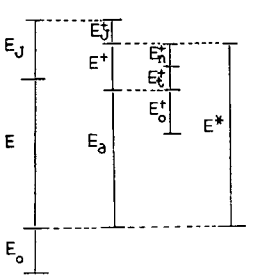

FIG. 1. Diagram of energy contributions to A* and A+.

Upon introducing (7) into (5) and integrating over J one finds

$$k_{\text{uni}}=\frac{kT}{h}\sum_g\frac{\alpha P_1^+\exp(-E_a/kT)}{P_1P_2\sigma_2^+} \times\int_{E^+=0}^{\infty}\frac{\sum_{E_n^+\leq E^+}W^+(E_n^+)\exp(-E^+/RT)}{1+(k_a/\omega)}\frac{dE^+}{kT}. \quad (9)$$

In (9) the properties of A+ (e.g., α, E_a, P_1^+, E_n^+, and σ_2^+) may depend on the path g.

The high-pressure value of k_{uni}, given by (10), is obtained from (9) by setting $\omega=\infty$ interchanging order of summation and integration ($E^+=E_n^+$ to ∞, and $E_n^+=0$ to ∞), integrating and summing:

$$\text{(high pressure) } k_{\text{uni}}=\frac{kT}{h}\sum_g\frac{\alpha P^+}{P}\exp\left(-\frac{E_a}{kT}\right). \quad (10)$$

Equations (7) (with $F=1$ and $\sum_g$ removed) and (9) can be shown to be equivalent to Eqs. (1) and (2) in Part II.[10] For recombination of methyl radicals and for recombination of NO_2 and NO_3 to form N_2O_5, F is about 0.8 and 0.4, respectively, at $E^*=E_a$, and is relatively insensitive to E^*.[11] Excellent approximations for $W^*(E^*)$ have been given in the literature [cf. Ref. (7b)].

In the case of an isomerization to form B from A, it may happen that the B* reforms A* before being deactivated. Equation (9) can easily be corrected to allow for such situations, by multiplying the numerator by $1-f$ and the k_a/ω in the denominator by $1-f$, where $f=k_a'/(k_a'+\omega)$. The term k_a' is the k_a for isomerization of B* to form an A*, and the derivation of this result is based on a steady-state approximation for both A* and B*. When k_a'/ω is small, f is negligible.

Parenthetically, we note that the analog of (10) can be derived for reactions in general,[4] thereby generalizing the usual activated-complex expression in the

[7] (a) In the semiclassical approximation for $W^*(x)$ a is unity (cf. Ref. 2). (b) A more accurate value for W^* has been obtained by making a slightly less than unity in such a way as to fit the exact numerical value of W^*. [B. S. Rabinovitch and R. W. Diesen, J. Chem. Phys. **30**, 735 (1959).] A very useful approximation for $W^*(x)$ has been given also by G. Z. Whitten and B. S. Rabinovitch, *ibid.* **38**, 2466 (1963). Compare Pearson and Rabinovitch, Ref. 2.

[8] The quantity s' equals $s+\frac{1}{2}t$, where s and t are the number of active vibrations and active rotations, respectively. (Compare Parts I and II.)

[9] Let the energy of the rotations that contribute appreciably to $E_J^+-E_J$ be ϵ_J and ϵ_J^+ for A and A+. The average value of $\epsilon_J^+-\epsilon_J$ is computed using the integrand of (9) as a weighting factor. The part of the weighting factor that depends on J is found to be $\exp(-\epsilon_J^+/kT)$ at very high pressures (high ω) and to be $W^*(E^*+\epsilon_J^+-\epsilon_J)\exp(-\epsilon_J^+/kT)$ at very low pressures. However, W^* depends on J much less than does $\exp(-\epsilon_J^+/kT)$, so that the weighting factor is essentially $\exp(-\epsilon_J^+/kT)$ in both cases and, indeed, over the entire range of pressures (i.e., of ω's). For these two rotations one then finds that $\langle\epsilon_J\rangle$, the value of ϵ_J averaged with the weighting factor $\exp(-\epsilon_J^+/kT)$, equals $(I^+/I)\ \langle\epsilon_J^+\rangle$. Since $\langle\epsilon_J^+\rangle=lRT/2$ the value cited in the text is obtained.

[10] The following data are used: For the two reactions, I^+/I is about 4, $l=2$, while E_a+aE_o is about 130 and 40 kcal mole^{-1}, respectively (taking $a\simeq 1$) and $s'-1$ is about 19 and 16, respectively. [See Part II and R. A. Marcus, J. Chem. Phys. **20**, 364 (1952).]

[11] A term

$$(\sigma_2^+)^{-1}\sum_{E_n^+\leq E^+}W^+(E^+)$$

contributing to (7) and (9) can be factored into terms corresponding to partitioning of E^+ among the active rotations and vibrations of A+:

$$(\sigma_2^+)^{-1}\sum_{E_n^+\leq E^+}W^+(E^+)=[P_R^+/(\tfrac{1}{2}r)!]\sum_{E_v^+\leq E^+}[(E^+-E_v^+)/RT]^{r/2}P(E_v^+),$$

where the symbols have been defined in Part II. We do not derive this equation since the derivation is similar to that employed in Part I for this phase of the problem. A quantity contributing to Eq. (7) is $W^*(E^*)/\sigma_2$, which represents the number of states per unit energy of the active modes. It was written as $N^*(E_a+E^++E_0)$ in Part II. Upon making this substitution and that given by this equation, Eqs. (1) and (2) of Part II are obtained.

literature and yielding (11):

$$k=(kT/h)\sum_g \alpha(P^+/P)\exp(-\Delta E_o^{\ddagger}/kT), \quad (11)$$

where $\Delta E_o^{\ddagger}$ is the energy of activation for path g at 0°K. This expression can be used to discuss statistical factors in reaction rates.[12] Equation (11) remains valid when quantum-rotational partition functions must be used. Alternative purely statistical expressions in the literature would of course become invalid then, since they are of classical origin. However, in cases of current interest the rotations are classical.

APPENDIX I. NOTATION

The following notation is employed, the energies being illustrated in Fig. 1.

A, A*, A^+	Reactant, active molecule (an A with enough energy to react), and the activated complex
E_a	Energy of A^+ in its lowest vibrational, rotational, and translational state minus that of A in its lowest state (hence, E_a also equals the activation energy at 0°K)
E, E^+	Energy of the "active" modes[3] of A* and of A^+ in excess of their zero-point energy, respectively
E_J, E_J^+	Energy of adiabatic modes[3] of A* and of A^+, respectively
q, p	Reaction coordinate and its conjugate momentum
E_t^+	Internal translational energy of A^+; $E_t^+=p^2/2m$
E_o, E_o^+	Zero-point energy of A, A^+
E_n^+	Energy of the active vibrations and rotations of an A^+ in Quantum State n
σ, σ^+	Symmetry numbers of A and A^+
σ_1, σ_1^+	Symmetry numbers for adiabatic rotations of A, A^+
σ_2, σ_2^+	Symmetry numbers of the other rotations
α	Number of optically isomeric reaction paths[4] for each geometrically different path leading from the initial A molecule (or A isomer if there is more than one) through A^+ to the given product
g	Label for a geometrically isomeric path
$\Omega^+(x)$, $\Omega^*(y)$	Number of states of active modes of A^+ formed by a given path and the number of states of A* (per unit energy in the case of A*), when the energy of the active modes is x and y, respectively, $\Omega^*=W^*/\sigma$, $\Omega^+=W^+/\sigma^+$
$W^+(x)$, $W^*(y)$	Number of such states of A^+ and A* when symmetry numbers are ignored
P, P^+	Partition function of rotational and vibrational modes of A and A^+, respectively, $P=P_1P_2$, $P^+=P_1^+P_2^+$
P_1, P_1^+	Partition functions of the adiabatic modes of A and of A^+
P_2, P_2^+	Partition functions of the active modes of A and of A^+
E^*	E_a+E^+
ω	Number of deactivating collisions which an A* undergoes per unit time

APPENDIX II. DERIVATION OF EQ. (3)

Consider an energetic molecule A* whose energy of the active modes is in an interval $(E, E+dE)$ and whose adiabatic modes are in a state J. The statistical equilibrium probability of finding such a molecule as an activated complex A^+ having an internal translational momentum in the range $(p, p+dp)$, being in a state n of the active modes and in an interval $(q, q+dq)$ and formed by a given path,[13] is given by the ratio of quantum states of this A^+ and of A*, namely by (A1), since $dqdp/h$ is the number of internal translational quantum states in $dqdp$:

$$(dqdp/h)\{\Omega^+(E_n^+)/[\Omega^*(E)dE]\}. \quad (A1)$$

The corresponding probability per unit interval along q is obtained by dividing by dq. The contribution of these states of A* to the specific unimolecular reaction-rate constant k_{EJ} is obtained by multiplying the resulting ratios by the velocity $\dot{q}$. The coordinate q is taken to be Cartesian, so that $\dot{q}$ equals p/m where m is an effective mass. Since $d(p^2/2m)$ equals dE, and since k_{EJ} equals the above rate expression summed over all accessible n (i.e., over $E_n^+\leq E^+$), we obtain

$$k_{EJ}=\sum_{E_n^+\leq E^+}\Omega^+(E_n^+)/[h\Omega^*(E)]. \quad (A2)$$

[In (A1) and (A2) the q motion is treated classically in the activated-complex neighborhood. A quantum treatment of this motion would introduce in (A2) a multiplicative factor κ, the quantum-mechanical transmission coefficient. See, for example, Ref. 4.] Equation (A2) is the contribution for a given reaction path. One must multiply it by the number of optical isomers of the path and then sum over the geometrical isomers of the path. Paths which are geometrically isomeric usually have different A^+'s, so in Eq. (3) we have summed over rather than multiplied by the number of such paths.

The $\Omega^+(E_n^+)$ and $\Omega^*(E)$ can be factored as follows: Because of symmetry restrictions some rotational states

[12] An alternative group theoretic description of the statistical effect has been given by E. W. Schlag, J. Chem. Phys. **38**, 2480 (1963); E. W. Schlag and G. L. Haller, *ibid.* **42**, 584 (1965). See D. M. Bishop and K. J. Laidler, *ibid.* p. 1688.

[13] In purely equilibrium calculations the path is of no concern. Kinetic calculations are based on some mechanistic path (e.g., see Ref. 4).

may be absent in A*, or in A^+ or in both. The coupling of vibrational and rotational angular momenta[14] facilitates the slight change of rotational state needed to satisfy such restrictions when A^+ is formed from A* or vice versa. On making the usual approximation employed in a classical description of rotational partition functions the absence of certain rotational states in A* or A^+ is accounted for by letting one factor in Ω^* be $1/\sigma$ and one in Ω^+ be $1/\sigma^+$.

[14] The total angular momentum, which is constant, has vibrational and rotational terms. [See E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill Book Company, Inc., New York, 1955), p. 277]. The coupling of these two contributions in the kinetic-energy expression permits some interchange, the equations of motion show.

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First and Second Triplets of Solid Benzene*

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Absorption spectra have been taken of the O_2-perturbed first ($^3B_{1u}$) and second ($^3E_{1u}$) triplets of solid benzene at 4.2°K. Spectra of both C_6H_6 and C_6D_6 were obtained. The (0–0) bands of the first triplet occur at 29 674±25 cm^{-1} for C_6H_6 and 29 851±25 cm^{-1} for C_6D_6. For the second triplet they lie at 36 560 cm^{-1}±50 for C_6H_6 and 36 784±50 cm^{-1} for C_6D_6. The result for the first triplet of C_6H_6 compares very favorably with Evans' gas-phase O_2-perturbed spectrum. It is also in satisfactory agreement with Nieman's accurate phosphorescence measurements on isotopic mixed crystals of benzene which place the C_6H_6 (0, 0) band position in the crystal at 29 657.1 cm^{-1}. Many precautions were taken to eliminate the possibility of mis identification of the second triplet. The observation that the O_2-enhanced first triplet and the O_2-enhanced bands in the 36 600-cm^{-1} region always appear together and with approximately the same relative intensities is considered to be the best evidence for the assignment. However, the rather broad structure obtained by the O_2-perturbation technique does not allow all the uncertainties in the identification to be completely removed, nor does it allow a detailed study of this interesting state.

A detailed evaluation of the purity of the benzene is made, and a method is described for the preparation of material having ultrahigh spectroscopic purity. Crystals, up to 5 cm in length, of this very highly purified C_6H_6 and C_6D_6 were studied at 4.2°K to ascertain if the singlet–triplet absorptions could be seen in the absence of a perturbation. The long crystals showed some sharp and some broad ($\Delta\nu \approx 150$ cm^{-1}) absorptions starting at 36 947±50 cm^{-1} in C_6H_6 and at 37 147±50 cm^{-1} in C_6D_6. The broad absorptions correlate reasonably well with the features assigned to the second triplet in the O_2-perturbation experiments. The first triplet is too weak to be observed in the long-crystal experiments. The position of the second triplet lies about 3000 cm^{-1} above that given by the Pariser–Parr calculation. This places the second triplet about nine-tenths rather than half of the distance from the lowest triplet to the lowest excited singlet.

INTRODUCTION

FOR many years the location of the second triplet state of benzene has been the object of much research, both theoretical and experimental.[1,2] This intense interest has been generated by theoretical predictions, many and varied, of the energies of the excited states of aromatic hydrocarbons. All theoretical predictions identify the second triplet of benzene as the orbitally degenerate $^3E_{1u}$ state, and most of these predictions place the second triplet in the experimentally accessible region between the lowest triplet and the lowest singlet.[3] Semiempirical theories[4,5] for these energy levels, which are based partially on spectral data, have seemed fairly promising. Thus it becomes of great importance to fix experimentally as many of the states of the lowest π–π^* manifold of benzene as possible. Up to now, all three singlet states, but only one triplet state, the lowest, have been identified.[6]

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[3] J. W. Moskowitz and M. P. Barnett, J. Chem. Phys. **39**, 1557 (1963); note that the use of a Goeppert-Mayer–Sklar core, accurate integrals, and extensive configuration interaction (Column *e* of Table I in this reference) places the second triplet *above* the first singlet.
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[5] H. E. Simmons, J. Chem. Phys. **40**, 3554 (1964).
[6] G. W. Robinson, in *Methods of Experimental Physics*, edited by D. Williams (Academic Press Inc., New York, 1962), Vol. 3, p. 244.